

1 **On the compositional variability of dalyite, $K_2ZrSi_6O_{15}$: a new**
2 **occurrence from Terceira, Azores**

3
4 A. J. Jeffery^{a*}, R. Gertisser^a, R. A. Jackson^a, B. O'Driscoll^{a, b}, A. Kronz^c

5
6 **a)** *School of Physical and Geographical Sciences, Keele University,*
7 *Keele, Staffordshire, ST5 5BG, United Kingdom*

8 **b)** *School of Earth, Atmospheric and Environmental Sciences, The*
9 *University of Manchester, Oxford Road, Manchester, M13 9PL*

10 **c)** *Geowissenschaftliches Zentrum Göttingen, Goldschmidtstrasse 3,*
11 *D-37077 Göttingen, Germany*

12
13 * Corresponding author:

14 *Tel.* +44 (0) 1782 733620

15 *E-mail* *a.j.jeffery@keele.ac.uk*

16
17 **Running title:** A new occurrence of dalyite, Azores

18

19 **Abstract**

20 The rare potassium zirconium silicate dalyite has been identified for the first time
21 on Terceira, Azores, within syenitic ejecta of the Caldeira-Castelinho Ignimbrite
22 Formation. New quantitative analyses of this dalyite are combined with the small
23 number of published analyses from various locations worldwide to evaluate the
24 mineral's compositional variability. Additionally, solid-state modelling has been
25 applied to assess the site allocations of substituting elements. The new analyses
26 yield the average formula $(K_{1.84}Na_{0.15})_{\Sigma=1.99}(Zr_{0.94}Ti_{0.012}Hf_{0.011}Fe_{0.004})_{\Sigma=0.967}Si_{6.03}O_{15}$.
27 Model results predict the placement of substituting Hf and Ti in the octahedral site,
28 and highlight the overall difficulty in the incorporation of Fe, Mg and Ba. The
29 combined dataset reveals that dalyite found within peralkaline granites and
30 syenites is generally defined by higher Na \leftrightarrow K substitution and lower Ti \leftrightarrow Zr
31 substitution relative to dalyite from highly potassic rocks. The Terceira dalyite
32 exhibits a bimodal variation in the degree of Na \leftrightarrow K substitution which is attributed
33 to a K-enrichment trend induced by late stage pore wall crystallisation and
34 albitization, coupled with the control of pore size upon the degree of
35 supersaturation required to initiate nucleation of dalyite in pores of varying size.

36

37

38 Key words: Dalyite, Peralkaline, Syenite, Oceanic island magmatism, Terceira,
39 Azores

40

41 **Introduction**

42 Dalyite is a rare potassium zirconium silicate, with the empirical formula $K_2ZrSi_6O_{15}$.
43 It was first identified in peralkaline granitic ejecta found within the pyroclastic
44 sequences of Green Mountain and Middleton Peak, Ascension Island (Van Tassel,
45 1952). Since its discovery, it has been identified as an accessory phase in a variety
46 of rocks, including peralkaline granites and syenites, late-stage pegmatites,
47 charoitites, lamproites, lamprophyres, fenites and carbonatites (e.g. Furnes et al.,
48 1982; Robins et al., 1983; Harris & Rickard, 1987; Linthout et al., 1988; Konev et

49 al., 1996). Having been established as a general indicator of peralkaline conditions,
50 silica-oversaturation, and high chemical potential of K_2O (μK_2O) (e.g. Marks et al.,
51 2011), the presence and composition of dalyite may provide important insights into
52 the evolution of these magmatic systems.

53 Here, we report the first known occurrence of dalyite from the mildly
54 peralkaline rocks of Terceira, Azores. We apply solid-state modelling to investigate
55 various proposed substituting elements, and complement the existing global
56 database with new high quality quantitative chemical analyses of dalyite from
57 Terceira. Using these analyses, alongside whole rock major element analyses of
58 the host syenites, we discuss the geochemical variability of dalyite, based on
59 previously published compositions from both similar and contrasting rock types.

60

61 **Background**

62 *Dalyite occurrences*

63 Following the initial discovery of dalyite (Van Tassel, 1952), it was next identified in
64 peralkaline syenitic ejecta from Agua de Pau volcano, São Miguel, Azores (Cann,
65 1967; Widom et al., 1993); where it was observed as an entirely intercumulus
66 phase and therefore inferred by Ridolfi et al. (2003) to be the last mineral to
67 crystallise (alongside quartz). Lazebnik & Makhotko (1982) identified dalyite in the
68 Murun Complex, Siberia, Russia, also providing additional quantitative analyses.
69 Furnes et al. (1982) and Robins et al. (1983) noted the presence of dalyite within a
70 highly potassic lamprophyric dyke in Sunnfjord, Norway. Raade & Mladeck (1983)
71 reported dalyite within a peralkaline granite pluton at Gjerdingen, Norway, where it
72 was typically found in close contact with janhaugite $Na_3Mn_3Ti_2Si_4O_{15}(OH,F,O)_3$.
73 Harris and Rickard (1987) recorded the occurrence of dalyite, alongside eudialyte,
74 in a peralkaline granitic dyke that cross-cuts the nepheline syenites of the
75 Straumsvola Complex, Antarctica. In 1988, an enstatite-sanidine-phlogopite
76 lamproite in south-eastern Spain was reported to contain the mineral's first known
77 occurrence in an extrusive rock (Venturelli et al., 1984; Linthout et al., 1988). Soon
78 afterwards, dalyite was observed within fenites from the Serra Negra and Salitre –
79 carbonatite alkaline igneous complex, Brazil (Mariano & Francis, 1989; Mariano &

80 Marchetto, 1991; Brod, 1999). Dalyite was later identified in the Strange Lake
81 peralkaline granite complex, Canada, and noted to have nucleated
82 heterogeneously onto older zircon crystals (Birkett et al., 1992; Salvi & Williams-
83 Jones, 1995). Subsequent reported occurrences include the Amis peralkaline
84 granite intrusion of the Brandberg Complex, Namibia (Schmitt et al., 2000), the
85 various lithologies of the Murun Complex, Siberia, Russia (e.g. Dolivo-
86 Dobrovol'skiy & Yevdokimov, 1991; Konev et al., 1996; Reguir, 2001), the Gordon
87 Butte pegmatites, Montana, USA (Chakhmouradian & Mitchell, 2002), peralkaline
88 granite dykes to the north of the Zargat Na'am ring complex, Egypt (Saleh, 2006),
89 more unusually, a nepheline-bearing pegmatite, Langesundfjord, Norway
90 (Andersen et al., 2010) and the alkali syenites and metasomatites of the
91 Shibanovsky Massif, Russia (Stepnova et al., 2013) (Fig. 1).

92 The occurrence documented here is within quartz syenite ejecta sampled
93 from the Caldeira-Castelinho Ignimbrite Formation (CCI) on Terceira Island, Azores
94 (Gertisser et al., 2010). The nine Azorean islands straddle the Mid-Atlantic Ridge in
95 the central North Atlantic Ocean and mark a triple junction between the American,
96 Eurasian and African plates (e.g. Krause & Watkins, 1970). All nine islands are
97 volcanic in origin and represent the subaerial manifestation of a large submarine
98 plateau, itself interpreted to have originated from the interaction of a mantle plume
99 with the Mid-Atlantic Ridge (e.g. Gente et al., 2003). The CCI is one of at least
100 seven ignimbrite formations found within the stratigraphy of Terceira (Self, 1974,
101 1976; Gertisser et al., 2010) and can be readily distinguished from its counterparts
102 by its relative abundance of quartz syenite ejecta (Gertisser et al., 2010). The
103 discovery of dalyite within these ejecta marks the mineral's second known
104 occurrence within the Azores archipelago.

105

106 *Mineral properties*

107 Van Tassel (1952) provided the first description of the physical properties,
108 chemical composition, unit cell and x-ray powder diffraction data of dalyite. It is a
109 triclinic, colourless mineral of moderate positive relief, exhibiting up to second order
110 interference colours. The unit cell was defined as $K_2ZrSi_6O_{15}$, though the potential

111 substitutions of Na for K, and Hf for Zr, were suggested. The chemical similarity
112 between dalyite and wadeite ($K_2ZrSi_3O_9$) was also noted. The original quantitative
113 chemical analysis of dalyite is reported in Table 1 (analysis 1).

114 The crystal structure of dalyite was determined by Fleet (1965), who
115 defined it as a phyllosilicate comprising four-, six- and eight-membered rings of
116 SiO_4 tetrahedra. These sheets are linked by regular ZrO_6 octahedra and irregular
117 $(K,Na)O_8$ polyhedra. Robins et al. (1983) provided 10 quantitative chemical
118 analyses of dalyite from Sunnfjord, Norway and presented evidence for the
119 substitution of Zr with Ti, and K with Fe, suggesting the more accurate empirical
120 formula $(K,Na,Fe)_2(Zr,Ti)Si_6O_{15}$. They also highlighted the compositional similarity
121 between dalyite and darapiosite, $KNa_2LiMnZnZrSi_{12}O_{30}$, sogdianite, (K,Na)
122 $_2Li_2(Li,Fe,Al,Ti)_2Zr_2(Si_2O_5)_6$ and zektzerite, $LiNaZrSi_6O_{15}$. Further chemical analyses
123 of dalyite were reported by Harris et al. (1982), Lazebnik & Makhotko (1982),
124 Harris & Rickard (1987), Linthout et al. (1988), Birkett et al. (1992), Konev et al.
125 (1996), Reguir (2001), Chakhmouradian & Mitchell (2002) and Ridolfi et al. (2003)
126 (Table 1).

127

128 **Methods**

129 *Analytical procedure*

130 Whole rock major element analyses of the syenite ejecta were undertaken at
131 Acme Analytical Laboratories Ltd, Canada, using x-ray fluorescence (XRF)
132 spectrometry (samples TER 30-1, TER 30-6, TER35-1), and inductively coupled
133 plasma atomic emission spectroscopy (ICP-AES) (TER 30-7). Weathered surfaces
134 were removed and samples were crushed in an agate mill, prior to drying for 2
135 hours at 110 °C and a $LiBO_2$ fusion. Loss-on-ignition (LOI) was reported as the
136 weight difference after ignition for 2 hours at 1,000 °C.

137 Semi-quantitative analyses and element maps were produced using a
138 Hitachi TM-3000 scanning electron microscope (SEM) equipped with a Bruker
139 Quantax 70 energy dispersive system (EDS) at Keele University, U.K. Quantitative
140 major element analyses of dalyite were achieved for samples TER 30-1 and TER

141 30-7 using a JEOL JXA 8900 RL electron microprobe at the Georg-August
142 Universität Göttingen, Germany. Peak counting times were 15 seconds for Si, Ti,
143 Al, Fe, Mg, Ca, Na and K, and 30 seconds for Cr, Zr, Hf, Mn and Ba, using an
144 acceleration voltage of 15 kV, a beam current of 15 nA and a 20 µm defocused
145 beam. The following natural silicate minerals and synthetic materials (denoted as
146 formulae) were used as primary standards: olivine (Si, Mg), albite (Na), sanidine
147 (K), TiO₂ (Ti), haematite (Fe), anorthite (Al), wollastonite (Ca), Cr₂O₃ (Cr), rhodonite
148 (Mn), celsian (Ba), ZrSiO₄ (Zr) and HfSiO₄ (Hf). Detection limits and errors (Table
149 2) were calculated at a confidence level of two-sigma from the raw background
150 noise and the signal/background counting, respectively, following the Gaussian law
151 of error propagation. The intensities were converted into concentrations by taking
152 the matrix corrections into account.

153

154 *Solid state modelling*

155 Solid state modelling calculations were carried out to investigate the substitution of
156 a number of potential substituting cations (Ti, Hf, Fe, Ba and Mg). This was
157 undertaken using the GULP code (Gale, 1997). This code uses effective
158 interatomic potentials to model the interactions between atoms, and has been
159 widely used to calculate the structure and properties of inorganic materials. The
160 Buckingham potential, supplemented by an electrostatic term, is used:

161

$$162 \quad V(r) = A \exp (-r/\rho) - Cr^{-6} + q_1q_2/r$$

163

164 In this equation, the parameters A, ρ and C are fitted to structures and properties of
165 related materials; here they have been transferred from studies on zircon (Akhtar &
166 Waseem, 2001). The charges of the interacting ions are q₁ and q₂. The
167 experimental and calculated lattice parameters for dalyite are given in Table 3
168 below, using the experimental structure from Fleet (1965) for comparison. It is seen
169 that the lattice parameters agree to within a few percent, which gives confidence in
170 using this transferred potential. The calculations reported here have been used to
171 obtain the energies involved when various ions are substituted into the dalyite

lattice. The calculation of substitutional and solution energies for dopant ions in materials has been widely described elsewhere; see, for example, a recent study of Nd, Gd and Yb ions in BaF₂ (Mujaji et al., 2014). However, a brief summary will be given here. In the case of the substitution of Ti⁴⁺ into the dalyite lattice, the following reaction (solution scheme) is considered, assuming substitution at the Zr⁴⁺ site:



The energy of this reaction (the solution energy), E_{sol} , is then calculated, as follows:

$$E_{\text{sol}} = [E_{\text{latt}}(\text{ZrO}_2) + E(\text{Ti}_{\text{Zr}})] - E_{\text{latt}}(\text{TiO}_2)$$

In this case no charge compensation is needed, but considering substitution at the K⁺ site, the following scheme was assumed (with charge compensation by K⁺ vacancies):



The solution energy for this reaction is:

$$E_{\text{sol}} = [E(\text{Ti}_\text{K}^{\bullet\bullet\bullet}) + 3E(\text{V}_\text{K}') + 2E_{\text{latt}}(\text{K}_2\text{O})] - E_{\text{latt}}(\text{TiO}_2)$$

In each case, a similar procedure is adopted, and a single solution scheme is assumed. More complex solution schemes, such as coupled substitutions, cannot be ruled out. Note that in the above expressions, Kröger-Vink notation has been used (Kröger & Vink, 1956).

Results

Petrography of the Caldeira-Castelinho Ignimbrite ejecta

Mineral assemblages of the CCI syenite ejecta include sodic alkali-feldspar, Na-pyroxene, Na-Ca to Na amphibole, quartz, aenigmatite and fayalite with accessory

202 Ti-magnetite, ilmenite, apatite, dalyite, an unspecified eudialyte group phase and
203 biotite. Significant grain-size variation exists between nodules, allowing the broad
204 distinction of two groups; fine to medium (~ 0.5 to 1.5 mm) grained nodules (Fig.
205 2a), and medium to coarse (~ 1.0 to 6.0 mm) grained nodules (Fig. 2b). Typically,
206 the fresher samples are more friable, whereas the more altered samples appear
207 more indurated. Some samples exhibit patches of granular texture, comprising
208 predominantly alkali-feldspar and quartz of finer grain size than the surrounding
209 material. Rarely, samples exhibit mineral modal and/or grain size layering at the
210 cm-scale.

211 Alkali-feldspar is by far the most abundant phase in all of the nodules and
212 ranges from fresh and unaltered crystals, to heavily altered, perthitic crystals.
213 Pyroxenes and amphiboles are the dominant intercumulus phases. Quartz is also
214 an intercumulus phase and is generally found as large rounded grains or
215 aggregates. Aenigmatite is typically present in small amounts and often exhibits a
216 complex reaction relationship with pyroxene, amphibole and Fe-Ti oxides. When
217 not associated with the apparent breakdown of aenigmatite, Fe-Ti oxides are
218 usually observed as inclusions within other phases (primarily alkali-feldspar).
219 Apatite exists as small, acicular inclusions within alkali-feldspars and varies in
220 abundance between samples. Dalyite is typically present as small (< 0.5 mm) sub-
221 to anhedral crystals (Fig. 2c-e), though can reach sizes of 1 to 1.5 mm (Fig. 2f). It is
222 almost exclusively anhedral and confined to the interstices, either filling or partially
223 filling void spaces. It is often associated spatially with quartz, and in some cases
224 can be found as inclusions within larger interstitial quartz crystals. An unspecified
225 eudialyte-group mineral is rarely found as frequently zoned anhedral crystals that,
226 like dalyite, appear to totally or partially infill interstitial pore spaces, and are often
227 spatially associated with clinopyroxene. Biotite is uncommon and, where present,
228 exists as small inclusions within alkali-feldspars.

229 *Whole rock and mineral compositions*

230 *Whole rock*

231 Four whole rock major element analyses of dalyite-bearing syenite nodules are
232 given in Table 4. Major element compositions are relatively uniform between
233 samples, with the variation of individual elements generally being restricted to less
234 than 1 wt. %. Peralkalinity indices and Na₂O/K₂O ratios range from 1.08 to 1.14
235 and 1.42 to 1.51, respectively. Calculated CIPW norms yield quartz, albite,
236 orthoclase, diopside, hypersthene, acmite, ilmenite, apatite and sodium
237 metasilicate. All samples are silica-oversaturated, with between 1.0 and 3.3 wt. %
238 normative quartz.

239

240 *Dalyite chemistry*

241 New chemical analyses of the CCI syenite dalyite (samples TER 30-1 and TER 30-
242 7) are reported in Table 5. The data reveal that the CCI syenite dalyite does not
243 deviate substantially from the empirical formula, with Na being the most significant
244 substituting element (~ 0.10 to 0.20 apfu), substituting for K. The combined totals
245 of atomic Na and K are close to the ideal total of 2 cations, and Fe contents are
246 often below detection limit (0.038 wt. %, average error = 0.052 wt. %), highlighting
247 limited incorporation of Fe in the dalyite structure. The low contents of Ti and Hf
248 (up to 0.030 and 0.013 apfu, respectively), indicate that replacement of Zr with Ti
249 and Hf is limited. These analyses suggest that the CCI dalyite corresponds to the
250 more precise formula (K_{1.79-1.87}Na_{0.12-0.19})(Zr_{0.90-0.96} Ti_{0.004-0.030}Hf_{0.010-0.013})(Si_{6.01-}
251 _{6.06}O₁₅). Calculated alkalinity moduli (Khomyakov 1995) values range from 21.90 to
252 22.39. In addition to Na, Fe Ti and Hf, the data suggest that trace amounts of Al,
253 Ba, Mg, and Mn may be present, though these are all very close to the detection
254 limit. This is supported by their occurrence in trace amounts in various literature
255 analyses (Table 1).

256

258 Calculated solution energies (E_{sol}) for a number of potential substitutions are
259 presented in Table 6. In each instance, the lowest E_{sol} value is considered to
260 highlight the most likely substitution. Model results for Ti indicate Ti \leftrightarrow Si substitution
261 as the most energetically favourable ($E_{\text{sol}} = -0.98$ eV), though Ti \leftrightarrow Zr substitution is
262 also likely ($E_{\text{sol}} = -0.25$ eV). Modelling of Hf is more conclusive, with Hf \leftrightarrow Zr
263 substitution representing the most likely scenario ($E_{\text{sol}} = -0.31$ eV). The
264 incorporation of the R^{2+} cations Fe^{2+} , Mg^{2+} and Ba^{2+} was also modelled, but charge
265 balancing necessitates the presence of site vacancies, in this case assumed to be
266 a single O vacancy. Results indicate that, in the case of Fe^{2+} and Mg^{2+} the lowest
267 energy scenario is replacement of K. Nevertheless, the calculated E_{sol} values of
268 8.86 eV and 9.61 eV, respectively, highlight the overall difficulty of their inclusion
269 within the dalyite structure. Modelling of Ba yields a similar result, though the
270 calculated E_{sol} value of 4.94 eV for Ba \leftrightarrow K substitution is noticeably lower than
271 other R^{2+} cations.

272 **Discussion**

273 *Variations in dalyite chemical composition*

274 To facilitate a wider discussion of the compositional variability of dalyite, all
275 available analyses are divided into two groups: 1) those found within peralkaline
276 syenitic or granitic rocks and 2) those found within other lithologies, including
277 lamproites, lamprophyres and charoitites. As such, the dalyite analyses from
278 Terceira, São Miguel, Ascension, Straumsvola, Strange Lake and Gordon Butte
279 are included in group 1, whereas analyses from Sunnfjord, Murun and Cancarix
280 occupy group 2. All analyses were tested for quality using the following criteria: a)
281 analysis total = 100 wt. % ± 1.5 , b) total cations = < 9.05 apfu, c) cation total for the
282 tetrahedral site = 6 apfu ± 0.05 , d) cation total for the octahedral site = 1 apfu \pm
283 0.05. Only those analyses which passed all four criteria were applied to the
284 following discussion, reducing the size of dataset from 43 to 25 analyses.

285 The overall average calculated K_{alk} for the combined dataset is 21.94, with
286 minimum and maximum values of 20.90 and 22.51, respectively. This shows

287 essentially no variation between groups 1 and 2, with average values of 21.98 and
288 21.91, respectively.

289 Figure 3a shows the available dalyite analyses in K–Na space. The data
290 typically lie within 0.05 apfu of the one-to-one line, indicating the role of one-to-one
291 $K \leftrightarrow Na$ substitution within the polyhedral sites. Group 1 analyses are characterised
292 by a relative abundance of Na (0.12 to 0.19 apfu) and a corresponding paucity of K
293 (1.79 to 1.87 apfu), though two analyses from Straumsvola and Strange Lake
294 (analyses 3 & 4, Table 1) exhibit Na concentrations below the detection limit,
295 alongside a slight deficiency in K. This discrepancy in older dalyite analyses may
296 indicate Na loss during analysis, as suggested by Birkett et al. (1992). The dalyite
297 from Strange Lake may also have been subject to alteration, as it is described as
298 being frequently rimmed by elpidite or vlasovite.

299 In contrast to group 1, group 2 analyses are closer to the ideal dalyite
300 formula, with significantly lower concentrations of Na (< 0.015 to 0.03 apfu). The
301 relatively sodic nature of group 1 and potassic nature of group 2 dalyite correlates
302 with the relatively sodic nature of the group 1 rocks and the generally potassic
303 nature of group 2 rocks. For example, reported whole rock Na_2O/K_2O ratios of
304 group 1 typically lie between 1 and 1.5 (Harris and Rickard, 1987; Ridolfi et al.,
305 2003; this study). In contrast, group 2 whole rock Na_2O/K_2O is likely to be
306 significantly lower, given their often highly potassic nature, as is the case for the
307 Cancarix dalyite ($Na_2O/K_2O = 0.1$, Linthout et al., 1988; Salvioli-Mariani &
308 Venturelli, 1996). Harris & Rickard (1987) made a similar observation, noting that
309 the dalyite analyses from Sunnfjord (analyses 16 to 25, Table 1) exhibit lower Na
310 contents than dalyite from Ascension Island (analysis 2, Table 1), which they
311 attributed to the higher Na_2O/K_2O ratio of the latter. However, they also noted that
312 Straumsvola dalyite (analysis 3, Table 1) has essentially no Na, despite a highly
313 comparable Na_2O/K_2O ratio to that of group 1 samples (1.35).

314 Another potential control that must be considered is the crystallisation
315 mechanism of each example, which must also play a role in the composition of
316 dalyite. For example, the dalyite-bearing, ultrapotassic Sunnfjord dyke is reported
317 to be heavily hydrothermally-altered (Furnes et al., 1982), suggesting that any
318 dalyite present may be metasomatic in origin, or a magmatic composition that has

319 been altered by metasomatism. It can be seen in Table 1 that those analyses
320 which may have been influenced by metasomatism (e.g. Sunnfjord, Murun)
321 frequently exhibit Na contents below detection. However, although the Straumsvola
322 analysis (itself an average of three analyses) contains no significant Na, the
323 peralkaline granite host rock is described as being very fresh (Harris & Rickard,
324 1987), and so the reported Na-poor dalyite cannot be attributed entirely to the
325 effects of crystallisation mechanism or alteration.

326 The degree of substitution within the octahedral sites is highlighted in
327 Figure 3b. Ti and Hf are considered as the most suitable substitutes, though the
328 R^{2+} cations Mg, Mn and Fe are also considered (where data is available), due to
329 the similarity of their ionic radii with Zr. In Figure 3b, the data plot within 0.05 apfu
330 of the one-to-one line, indicating one-to-one cation exchange. In the case of Fe,
331 Mn and Mg, this would introduce a charge imbalance which can be mitigated by a
332 single oxygen vacancy. Although solid-state modelling suggests that $R^{2+} \leftrightarrow K$
333 substitution should be energetically favourable, the calculated E_{sol} values are still
334 too large (8.86 eV & 9.61 eV), and the difference in ionic radii too great, to fully
335 justify the placement of R^{2+} cations in the polyhedral sites. The substitutions of
336 $Hf \leftrightarrow Zr$ and $Ti \leftrightarrow Zr$ are both supported by solid-state modelling ($E_{sol} = -0.31$ eV & -
337 0.25 eV, respectively, though in the latter case, the modelling also indicates the
338 potential of $Ti \leftrightarrow Si$ substitution ($E_{sol} = -0.98$ eV). However, there is no evidence
339 within the dataset to support such a substitution.

340 Group 1 analyses remain close to the ideal dalyite formula, with 0.91 to
341 0.98 apfu Zr. Group 2 analyses exhibit a greater degree of substitution, generally
342 clustering between 0.85 and 0.94 apfu Zr, with 0.05 to 0.12 apfu Ti. It is notable
343 that one of the two analyses from the charoitites of the Murun Complex is enriched
344 in the davanite component ($K_2TiSi_6O_{15}$), with 0.21 apfu Ti. This may relate to the
345 unusual nature of their charoititic host rock, which is typically considered to be
346 metasomatic rather than magmatic in origin (e.g. Reguir, 2001 and references
347 therein). This alternative origin may explain the apparent geochemical deviation
348 from the rest of the dataset.

349 The dataset indicates the presence of small amounts of Ba within Group 2
350 dalyite. On the basis of solid-state modelling and ionic radii, it is suggested that the

351 most likely mechanism for its inclusion within the dalyite structure is $Ba \leftrightarrow K$. The
352 resulting charge imbalance could be mitigated by a single vacancy in the
353 polyhedral site, in which case the Ba content may be used as a proxy for the
354 polyhedral vacancies in each analysis (up to 0.02 apfu). This may, in part, account
355 for analyses in which the structural total is less than the ideal 9 apfu. Alternatively,
356 structural deficits may result from the presence of Li. Significant concentrations of
357 Li have been reported in peralkaline rocks and Li-enrichment can occur via
358 metasomatic processes (e.g. Borley, 1963; Hawthorne et al., 1996; Brenan et al.,
359 1998; Hawthorne et al., 2001). Although the mechanisms of Li-substitution in
360 dalyite are unclear, its inclusion may contribute to the frequently low structural
361 totals observed within the dataset.

362 The key geochemical parameters required to stabilise dalyite are
363 high μK_2O and high $aSiO_2$ (Marks et al., 2011). For example, an insufficiently high
364 silica activity will lead to the crystallisation of wadeite ($K_2ZrSi_3O_9$) in place of dalyite
365 (Marks et al., 2011). Dalyite is therefore limited to silica-saturated to –oversaturated
366 lithologies, although its occurrence in a nepheline-bearing pegmatite from
367 Langesundfjord, Norway (Andersen et al., 2010) appears to contradict this. The
368 additional requirement of high μK_2O is likely due to high K_2O contents in the melts,
369 achieved either by slowly increasing K_2O via fractional crystallisation and/or crustal
370 assimilation of potassic rocks in the group 1 samples, or by producing melts with
371 initially high K_2O values via the more unusual processes suggested to produce
372 ultrapotassic rocks, such as partial melting of metasomatised mantle lithologies,
373 (e.g. Mitchell & Bergman, 1991).

374 The geochemical variations observed between the groups of this study are
375 likely to represent major element variations in the melts themselves. For example,
376 the group 2 dalyites generally show elevated Ti and Fe contents relative to the
377 group 1 dalyites, which may relate to the relatively Ti- and Fe-rich whole rock
378 compositions of lamproites and lamprophyres, particularly when compared to the
379 low Ti contents of group 1 whole rock analyses (< 0.7 wt. %). Additionally, group 2
380 analyses exhibit significantly lower degrees of Na substituting for K, which might be
381 expected given the K_2O -rich nature of their whole rock analyses.

382

383 *Dalyite crystallisation on Terceira*

384 Dalyite is generally considered to be a late-stage, magmatic mineral phase (e.g.
385 Harris & Rickard, 1987; Ridolfi et al., 2003) that may be altered, either during later
386 magmatic or sub-solidus stages, to minerals such as elpidite, $\text{Na}_2\text{ZrSi}_6\text{O}_{15}\cdot 3(\text{H}_2\text{O})$
387 (Cann, 1967), catapleiite, $\text{Na}_2\text{Zr}(\text{Si}_3\text{O}_9)\cdot 2\text{H}_2\text{O}$ (Birkett et al., 1992; Chakhmouradian
388 & Mitchell, 2002) and intergrown quartz and zircon (Cann, 1967). Key features of
389 the Terceira dalyite, notably the dominantly anhedral crystal forms, its restricted
390 occurrence in interstitial pore spaces and its lack of inclusion within other mineral
391 phases, all point towards late-stage, post-cumulus, magmatic crystallisation,
392 though extension of the crystallisation interval into the sub-solidus deuteric stage
393 cannot be ruled out. Evidence for the alteration of primary dalyite compositions is
394 lacking. Its textural association and occasional intergrowth with quartz suggests
395 that the crystallisation of these two phases was largely contemporaneous. This
396 conclusion is in agreement with that of Ridolfi et al. (2003), who studied similar
397 parageneses in syenite nodules erupted by Agua de Pau volcano, São Miguel,
398 Azores.

399 The dalyite analyses from Terceira display two clusters in Na-K space (Fig.
400 3a), with one cluster of more sodic compositions (0.17 to 0.19 Na apfu), and
401 another cluster of more potassic compositions (0.12 to 0.13 Na apfu). The
402 difference between these clusters cannot be entirely accounted for by the
403 calculated two-sigma errors of ± 0.015 apfu, and is considered to represent
404 bimodality in the dataset. Both clusters lie within 0.05 apfu of the one-to-one line
405 and, as such, the trend of the data likely highlights the role of varying degrees of
406 one-to-one $\text{Na}\leftrightarrow\text{K}$ substitution within the Terceira samples. The presence of two
407 subgroups may imply that two separate populations of dalyite are present, either
408 derived from multiple processes that each led to the crystallisation of
409 compositionally distinct dalyite, or a single process that is capable of producing a
410 heterogeneous dalyite population. No visible correlation exists between dalyite
411 composition and textural features such as crystal form or size, or the degree to
412 which they infill pores. Instead, the two clusters of dalyite analyses can be related
413 to the two separate samples in which dalyite was analysed (TER-30-1 and TER 30-

7), with the most sodic dalyite analyses being from TER 30-1. The compositional variations may therefore reflect random sampling of a syenitic mush in which geochemical heterogeneity is sufficiently large in scale that it yields 'inter-nodule' variations in dalyite composition, whilst 'intra-nodule' variations are more limited. Such heterogeneity may be primary (i.e. derived from original compositional variations in the melt, perhaps originating from multiple magma batches that contributed to a single crystal mush body), or secondary, originating from the variable degree of fluid-feldspar reaction (albitization; e.g. Lee & Parsons, 1997) in the crystal mush during deuteric alteration. The late stage albitization of the rock would lead to a bulk rock increase in Na and an enrichment of K in the albitizing fluids. The prevalence of coarse patchy perthitic feldspars in the Terceira syenites provides evidence for the prominent role of albitization in their late stage evolution. Evidence for primary bulk compositions being the underlying control upon dalyite composition exists in the bimodality of the dataset, with the most sodic dalyites found in the most sodic whole rock analysis.

However, a single analysis from sample TER 30-7 falls within the cluster of TER 30-1 analyses (Fig. 2a, Table 5), indicating that a simple relationship between dalyite chemistry and bulk rock composition cannot entirely account for the observed variation. As such, alternative processes that might influence the degree of Na \leftrightarrow K substitution are explored. One example that is considered here is the role of variable pore size in the compositional evolution of interstitial melts. Because heterogeneous nucleation is energetically favourable compared to homogenous nucleation, the dominant process that drives the compositional evolution of a melt within a pore under closed system conditions is the crystallisation of surrounding cumulus phases, as components that are incompatible in the pore wall minerals become enriched in the residual melt. In the Terceira syenite nodules, alkali-feldspar is the most abundant phase, and surrounds the majority of pore spaces, suggesting that the post-cumulus, heterogeneous nucleation of feldspar onto pore walls will exert the strongest influence upon interstitial melt compositions. Due to its albite-rich composition (\sim Ab₆₄, average Na/K = 1.67) (A. J. Jeffery, unpublished data), this effect is likely to promote the development of depressed Na/K ratios in the liquid as evolution continues. Petrographic evidence for this process exists in

446 the form of optically distinguishable rims on many of the pore-wall feldspars (e.g.
447 Fig. 2c). During the sub-solidus deuteric stage, albitization also contributes to the
448 depression of liquid Na/K ratios via the replacement of alkali feldspar with near end
449 member albite. Thus, it is suggested that during the late stage magmatic and sub-
450 solidus deuteric evolution of the syenite, the majority of liquid-filled pores were
451 evolving towards more potassic compositions.

452 It is proposed that the observed variation in Terceira dalyite composition
453 could be related to the timing of crystallisation relative to the evolution of the
454 interstitial melt. The thermodynamics of crystallisation in pore spaces has been
455 shown to be fundamentally different compared to a free fluid (Bigg, 1953; Melia &
456 Moffitt, 1964; Putnis et al., 1995; Scherer, 1999). In particular, a fluid confined to a
457 pore space can achieve greater degrees of supersaturation prior to the onset of
458 crystallisation compared with an unconfined fluid, thus introducing a nucleation
459 delay that is more substantial in smaller pores (e.g. Putnis & Mauthe, 2001;
460 Holness et al., 2007; Holness & Sawyer, 2008). As such, the dalyite crystals that
461 grew in smaller pores would have nucleated later than those in larger pores, and
462 would record more evolved compositions. Holness & Sawyer (2008) also cited the
463 prevalence of single-grain pseudomorphs in small pores and poly-mineralic
464 aggregate pseudomorphs in larger pores as petrographic evidence for the relative
465 ease of nucleation in larger pores. This feature can also be observed in the CCI
466 syenite, where larger pores are frequently filled with aggregates of late-crystallising
467 phases such as quartz, clinopyroxene, dalyite, and eudialyte (Fig. 2f), whilst small
468 pores generally contain only a single crystal of one of these phases (Fig. 2d).

469 Considering the previously described evolutionary trend of relative K-
470 enrichment during both late stage magmatic and sub-solidus stages, dalyite in
471 smaller pores should therefore have more potassic compositions. To test this
472 hypothesis, dalyite-bearing pore spaces were digitised and measured using
473 ImageJ to determine the two-dimensional area. This was then plotted against the
474 Na content of the dalyite crystal within them (Fig. 4), yielding a positive correlation
475 that suggests that the size of a pore exerts, at least to some extent, a control over
476 the composition of the dalyite crystallising within it.

477 A single data point in Fig. 4 appears to deviate from the broadly linear
478 trend observed in the rest of the data (pore area = 1.07 mm^2 , Na content = 0.18).
479 Unlike other reported dalyites, this dalyite crystal is found in a pore that is bounded
480 by a large clinopyroxene crystal, in addition to alkali-feldspar. It is therefore
481 suggested that this deviation in pore size vs. Na content space may highlight the
482 influence of other minerals in the evolution of interstitial melts. Given the relatively
483 high Na contents and negligible K contents of the Terceira clinopyroxene (Na/K = 6
484 to 2584) (A. J. Jeffery, unpublished data), the pore wall crystallisation of
485 clinopyroxene would greatly accelerate the described evolutionary trend of K-
486 enrichment in interstitial melt, leading to dalyite compositions that appear unusually
487 K-rich when compared with the suggested feldspar-controlled trend (Fig. 4). The
488 pore wall crystallisation of amphibole would also produce this effect but to a lesser
489 degree (Na/K = 5.7 to 8.9) (A. J. Jeffery, unpublished data).

490 In summary, it is suggested that the dalyite from Terceira is predominantly
491 late-stage magmatic in origin, and the observed compositional variability is
492 influenced by the K-enrichment trend of late stage interstitial melt resulting from
493 pore wall crystallisation of sodic alkali feldspar. Any continued crystallisation during
494 a sub-solidus deuteric stage is considered to have been subject to a similar K-
495 enrichment trend, driven by albitization of alkali feldspar. Variation in Na content is
496 likely to have been controlled, at least in part, by the larger nucleation delay that is
497 introduced in smaller pores compared to larger ones.

498

499 **Conclusions**

500 A new occurrence of the rare potassium zirconium dalyite is reported from
501 Terceira, Azores. The detailed study of new quantitative analyses of dalyite from
502 Terceira, alongside solid state modelling and previously published analyses, allows
503 the following conclusions to be made regarding the compositional variability of
504 dalyite:

- 505 (1) Substitution of Na for K in dalyite is generally more significant in
506 peralkaline granites and syenites than in highly potassic rock types.

- 507 (2) The incorporation of small amounts of Ba occurs in potassic rocks and is
508 most likely achieved via Ba \leftrightarrow K substitution..
- 509 (3) The incorporation of Fe into dalyite is minimal in peralkaline granites and
510 syenites, but becomes more significant in highly potassic lithologies.
511 Mineral chemical data and solid state modelling suggest that this is most
512 easily achieved via Fe²⁺ \leftrightarrow Zr substitution, though high E_{sol} values and
513 charge balancing requirements must hinder this relationship.
- 514 (4) The degree of substitution of Ti for Zr is greater in highly potassic igneous
515 rocks than in peralkaline granites and syenites, and may be linked to
516 elevated Ti-contents of the melts.
- 517 (5) The dalyite from Terceira shows variation in the degree of Na \leftrightarrow K
518 substitution that does not relate obviously to texture, and cannot be entirely
519 attributed to 'inter-nodule' diversity. This feature is linked to relative K-
520 enrichment induced by the effects of pore wall crystallisation (during a late
521 stage magmatic phase) and albitization (during a sub-solidus deuteric
522 phase), coupled with the variation in nucleation delay that is introduced by
523 variable pore sizes.

524

525 **Acknowledgements**

526 We gratefully acknowledge S. Self, A. Pimentel, J. Pacheco and the Centro de
527 Vulcanologia e Avaliação de Riscos Geológicos (CVARG) for their invaluable
528 assistance and logistical support during fieldwork. We are grateful to P. Williams
529 and R. Mitchell for editorial handling, and F. Ridolfi and G. Gatta for their detailed
530 and constructive comments, which greatly improved the manuscript. E. Reguir is
531 thanked for kindly providing a copy of Table 48 from Konev et al. (1996).

532

533

534 **References**

- 535 Akhtar, M. J., Waseem, S. (2001) Atomistic simulation studies of zircon. Chemical
536 Physics, 274: 109-120
537
- 538 Andersen, T., Erambert, M., Larsen, A. O., Selbekk, R. S. (2010) Petrology of
539 nepheline syenite pegmatites in the Oslo Rift, Norway: zirconium silicate mineral
540 assemblages as indicators of alkalinity and volatile fugacity in mildly agpaitic
541 magma. Journal of Petrology, 51: 2303-2325
542
- 543 Bigg, E. K. (1953) The supercooling of water. Proceedings of the Physical Society
544 (London), 66B: 688-694
545
- 546 Birkett, T. C., Miller, R. R., Roberts, A. C., Mariano, A. N. (1992) Zirconium-bearing
547 minerals of the Strange Lake Intrusive Complex, Quebec-Labrador. Canadian
548 Mineralogist, 30: 191-205
549
- 550 Borley, G. D. (1963) Amphiboles from the Younger Granites of Nigeria. I. Chemical
551 classification. Mineralogical Magazine, 33: 358-376
552
- 553 Brenan, J. M., Neroda, E., Lundstrom, C. C., Shaw, H. F., Ryerson, F. J., Phinney,
554 D. L. (1998) Behaviour of boron, beryllium, and lithium during melting and
555 crystallization: constraints from mineral-melt partitioning experiments. Geochimica
556 et Cosmochimica Acta, 62: 2129-2141
557
- 558 Brod, J. A. (1999) Petrology and geochemistry of the tapira alkaline complex,
559 minas gerais state, Brazil. [Ph.D. thesis]. Durham University, U.K., 486 pp.
560
- 561 Cann, J. R. (1967) A second occurrence of dalyite and the petrology of some
562 ejected syenite blocks from São Miguel, Azores. Mineralogical Magazine, 36: 227-
563 232
564

565 Chakhmouradian, A. R., Mitchell, R. H. (2002) The mineralogy of Ba- and Zr-rich
 566 alkaline pegmatites from Gordon Butte, Crazy Mountains (Montana, USA):
 567 comparisons between potassic and sodic agpaitic pegmatites. Contributions to
 568 Mineralogy and Petrology, 143: 93-114
 569
 570 Dolivo-Dobrovol'skiy, D. V., Yevdokimov, M. D. (1991) Zirconium mineralisation of
 571 the alkali metasomatites of the Murun Complex. International Geology Review, 33:
 572 490-496
 573
 574 Fleet, S. G. (1965) The crystal structure of dalyite. Zeitschrift für Kristallographie,
 575 121: 349-368
 576
 577 Furnes, H., Mitchell, J. G., Robins, B., Ryan, P., Skjerlie, F. J. (1982) Petrography
 578 and geochemistry of peralkaline, ultrapotassic syenite dykes of Middle Permian
 579 age, Sunnfjord, West Norway. Norsk Geologisk Tidsskrift, 62: 147-159
 580
 581 Gale, J. D. (1997) GULP: A computer program for the symmetry-adapted
 582 simulation of solids. Journal of the Chemical Society, Faraday Transactions, 93:
 583 629-637
 584
 585 Gente, P., Dymant, J., Maia, M., Goslin, J. (2003) Interaction between the Mid-
 586 Atlantic Ridge and the Azores hot spot during the last 85 Myr: emplacement and
 587 rifting of the hotspot derived plateaus. Geochemistry, Geophysics, Geosystems, 4:
 588 8514, doi: 10.1029/2003GC000527
 589
 590 Gertisser, R., Self, S., Gaspar, J. L., Kelley, S. P., Pimentel, A., Eikenberg, J.,
 591 Barry, T. L., Pacheco, J. M., Queiroz, G., Vespa, M. (2010) Ignimbrite stratigraphy
 592 and chronology on Terceira Island, Azores. The Geological Society of America,
 593 Special Paper 464: 133-154
 594

595 Harris, C., Cressey, G., Bell, J. D., Atkins, F. B., Beswetherick, S. (1982) An
 596 occurrence of rare-earth-rich eudialyte from Ascension Island, South Atlantic.
 597 Mineralogical Magazine, 46: 421-425
 598
 599 Harris, C., Rickard, R. S. (1987) Rare-earth-rich eudialyte and dalyite from a
 600 peralkaline granite dyke at Straumsvola, Dronning Maud Land, Antarctica. The
 601 Canadian Mineralogist, 25: 755-762
 602
 603 Hawthorne, F. C., Oberti, R., Ottolini, L., Foord, E. E. (1996) Lithium-bearing fluor-
 604 arvedsonite from Hurricane Mountain, New Hampshire: a crystal-chemical study.
 605 The Canadian Mineralogist, 34: 1015-1019
 606
 607 Hawthorne, F. C., Oberti, R., Cannillo, E., Ottolini, L., Roelofsen, J. N., Martin, R. F.
 608 (2001) Li-bearing arvedsonitic amphiboles from the Strange Lake peralkaline
 609 granite, Quebec. The Canadian Mineralogist, 39: 1161-1170
 610
 611 Holness, M. B., Anderson, A. T., Martin, V. M., MacLennan, J., Passmore, E.,
 612 Schwindinger, K. (2007) Textures in partially solidified crystalline nodules: a
 613 window into the pore structure of slowly cooled mafic intrusions. Journal of
 614 Petrology, 48: 1243-1264
 615
 616 Holness, M. B., Sawyer, E. W. (2008) On the pseudomorphing of melt-filled pores
 617 during crystallization of migmatites. Journal of Petrology, 49: 1343-1363
 618
 619 Khomyakov, A. P. (1995) Mineralogy of hyperagpaitic alkaline rocks. Oxford
 620 Science Publications, Oxford, UK. 222 pp.
 621
 622 Konev, A. A., Vorob'ev, E. I., Lasebnik, K. A. (1996) The mineralogy of the Murun
 623 alkaline massif. Siberian Branch of the Russian Academy, Scientific Press,
 624 Novosibirsk, (in Russ.)
 625

626 Krause, D. C., Watkins, N. D. (1970) North Atlantic crustal genesis in the vicinity of
627 the Azores. *Geophysical Journal of the Royal Astronomical Society*, 19: 261-283
628

629 Kröger, F. A., Vink, H. J. (1956) Relations between the concentrations of
630 imperfections in crystalline solids. *Solid State Physics*, 3, 307-435
631

632 Lazebnik, K. A., Makhotko, V. F. (1982) Dalyite, the first finding in the USSR.
633 *Zapiski Vsesoyuznogo Mineralogicheskogo Obschestva*, 111: 587-593
634

635 Lee, M. R., Parsons, I. (1997) Dislocation formation and albitization in alkali
636 feldspars from the Shap granite. *American Mineralogist*, 82: 557-570
637

638 Linthout, K., Nobel, F. A., Lustenhouwer, W. J. (1988) First occurrence of dalyite in
639 extrusive rock. *Mineralogical Magazine*, 52: 705-708
640

641 Mariano, A. N., Francis, C. A. (1989) Dalyite from fenites in carbonatite complexes
642 of the Minas Gerais – Goiás belt, Brazil. *Geological Society of America Abstract*
643 *Programs*, 21: A46
644

645 Mariano, A. N., Marchetto, M. (1991) Serra Negra and Salitre – carbonatite alkaline
646 igneous complex. In: Leonardos, O. H., Meyer, H. O. A., Gaspar, J. C. (Eds) 5th
647 *International Kimberlite Conference (Field Guide Book)*. Araxá, Brazil, CPRM,
648 *Special publication*, 3/91: 75-79
649

650 Marks, M. A. W., Hettmann, K., Schilling, J., Frost, B. R., Markl, G. (2011) The
651 mineralogical diversity of alkaline igneous rocks: critical factors for the transition
652 from miaskitic to agpaitic phase assemblages. *Journal of Petrology*, 52: 439-455
653

654 Melia, T. P., Moffitt, W. P. (1964) Crystallisation from aqueous solution. *Journal of*
655 *Colloid Science*, 19: 433-447
656

657 Mitchell, R. H., Bergman, S. C. (1991) Petrology of lamproites. New York/London:
658 Plenum Press. 447 pp.
659

660 Mujaji, M., Burrows, J., Jackson, R. A. (2014) Optical spectroscopy of the Nd^{3+} and
661 Nd^{3+} - $\text{Gd}^{3+}/\text{Yb}^{3+}$ centres in BaF_2 single crystals and calculations on lanthanide-
662 doped BaF_2 . Journal of Luminescence, 151: 106-110
663

664 Putnis, A., Mauthe, G. (2001) The effect of pore size on cementation in porous
665 rocks. Geofluids, 1: 37-41
666

667 Putnis, A., Prieto, M., Fernandez-Diaz, L. (1995) Supersaturation and
668 crystallisation in porous media. Geological Magazine, 132: 1-13
669

670 Raade, G., Mladeck, M. H. (1983) Janhaugite, $\text{Na}_3\text{Mn}_3\text{Ti}_2\text{Si}_4\text{O}_{15}(\text{OH},\text{F},\text{O})_3$, a new
671 mineral from Norway. American Mineralogist, 68: 1216-1219
672

673 Reguir, E. (2001) Aspects of the mineralogy of the Murun alkaline complex,
674 Yakutia, Russia. [M.Sc thesis]. Lakehead University, Canada, 193 pp.
675

676 Ridolfi, F., Renzulli, A., Santi, P., Upton, B. G. J. (2003) Evolutionary stages of
677 crystallization of weakly peralkaline syenites: evidence from ejecta in the plinian
678 deposits of Agua de Pau volcano (Sao Miguel, Azores Islands). Mineralogical
679 Magazine, 67: 749-767
680

681 Robins, B., Furnes, H., Ryan, P. (1983) A new occurrence of dalyite. Mineralogical
682 Magazine, 47: 93-94
683

684 Saleh, G. M. (2006) Geologic relationships and mineralisation of
685 peralkaline/alkaline granite-syenite of the Zargat Na'am ring complex,
686 Southeastern Desert, Egypt. Chinese Journal of Geochemistry, 25: 97-111
687

688 Salvi, S., Williams-Jones, A. E. (1995) Zirconosilicate phase relations in the
689 Strange Lake (Lac Brisson) pluton, Quebec-Labrador, Canada. *American*
690 *Mineralogist*, 80: 1031-1040
691

692 Salvioli-Mariani, E., Venturelli, G. (1996) Temperature of crystallisation and
693 evolution of the Jumilla and Cancarix lamproites (SE Spain) as suggested by melt
694 and solid inclusions in minerals. *European Journal of Mineralogy*, 8: 1027-1039
695

696 Scherer, G. W. (1999) Crystallization in pores. *Cement and Concrete Research*,
697 29:1347-1358
698

699 Schmitt, A. K., Emmermann, R., Trumbull, R. B., Bühn, B., Henjes-Kunst, F. (2000)
700 Petrogenesis and $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology of the Brandberg Complex, Namibia:
701 evidence for a major mantle contribution in metaluminous and peralkaline granites.
702 *Journal of Petrology*, 41: 1207-1239
703

704 Self, S. (1974) Recent volcanism on Terceira, Azores. [Ph.D. thesis]. Imperial
705 College, U.K., 236 pp.
706

707 Self, S. (1976) The recent volcanology of Terceira, Azores. *Journal of the*
708 *Geological Society*, 132: 645-666
709

710 Stepanova, Y. A., Zalizchak, B. L., Pakhomova, V. A. (2013) Rare-earth
711 mineralisation of alkali magma of the Russian Far East: on the example of the
712 Shibanovsky massif. *Геология, Вестник*, 3: 44-51 (in Russ.)
713

714 Van Tassel, R. (1952) Dalyite, a new potassium zirconium silicate, from Ascension
715 Island, Atlantic. *Mineralogical Magazine*, 29: 850-857
716

717 Venturelli, G., Capedri, S., Di Battistini, G., Crawford, A., Kogarko, L. N., Celestini,
718 S. (1984) The ultrapotassic rocks from southeastern Spain. *Lithos*, 17: 37-54
719

720 Widom, E., Gill, J. B., Schmincke, H. -U. (1993) Syenite nodules as a long-term
721 record of magmatic activity in Agua de Pau volcano, São Miguel, Azores. Journal
722 of Petrology, 34: 929-953

Figure captions

Figure 1 Reported occurrences of dalyite worldwide. **1)** Ascension Island, South Atlantic Ocean (Van Tassel, 1952) **2)** Agua de Pau volcano, São Miguel, Azores (Cann, 1967) **3)** the Murun Complex, Siberia, Russia (Lazebnik & Makhotko, 1982; Dolivo-Dobrovol'skiy & Yevdokimov, 1991; Konev et al., 1996; Reguir, 2001) **4)** Gjerdingen, Norway (Raade & Mladeck, 1983) **5)** Sunnfjord, Norway (Furnes et al., 1982; Robins et al., 1983) **6)** the Straumsvola Complex, Dronning Maud Land, Antarctica (Harris & Rickard, 1987) **7)** Cancarix, South Eastern Spain (Venturelli et al., 1984; Linthout et al., 1988) **8)** the Serra Negra and Salitre Complex, Brazil (Mariano & Francis, 1989; Mariano & Marchetto, 1991) **9)** the Strange Lake Complex, Canada (Birkett et al., 1992; Salvi & Williams-Jones, 1995) **10)** the Brandberg Complex, Namibia (Schmitt et al., 2000) **11)** Gordon Butte, Montana, USA (Chakhmouradian & Mitchell, 2002) **12)** the Zargat Na'am ring complex, Egypt (Saleh, 2006) **13)** Langesundfjord, Norway (Andersen, et al., 2010) **14)** the Shibanovsky Massif, Russia (Stepnova et al., 2013) **15)** Terceira Island, Azores (this study)

Figure 2 a) Example of a fine to medium grained, alkali-feldspar dominated nodule. The feldspars appear altered and are often perthitic. A large, optically-continuous quartz crystal is highlighted with a white box in the lower right corner of the image. **b)** A medium to coarse grained nodule with larger crystal sizes and fresher, less-altered feldspars **c)** A large dalyite crystal which partially infills an interstitial void between larger alkali-feldspar crystals. Also visible are small amphibole crystals and stellate clinopyroxene **d)** An anhedral dalyite crystal which partially fills an interstitial void between large alkali-feldspars and a large amphibole crystal **e)** An anhedral dalyite crystal forming an incomplete rim around the edges of an interstitial cavity. A small clinopyroxene crystal appears to have been included within the dalyite. A resorbed, optically distinctive feldspar core is visible within the large feldspar to the lower right of the image **f)** An element map highlighting a large, anhedral dalyite crystal filling an interstitial space, together with intergrown quartz and small amounts of clinopyroxene. Colours used: Red = Fe, Purple = Zr, Blue = Si, Green = Al. Abbreviations used: Qtz = quartz, Fsp = alkali-feldspar, Amp = amphibole, Cpx = Clinopyroxene, Dal = dalyite

Figure 3 Geochemical variation diagrams highlighting the variable degree of substitution within the dataset. The ideal composition of dalyite is highlighted with a black star symbol. The maximum error is applicable to the new data for Terceira (TER 30-1 and TER 30-7) only and is calculated as described in the text. Group 1 dalyite is denoted by diamonds, group 2 by triangles. Only analyses that passed all of the filtering criteria described in the text are shown

a) Bivariate plot showing the degree of $K \leftrightarrow Na$ substitution in the dataset. **b)** Bivariate plot showing the degree of substitution in the octahedral site. Data for Hf, Mg and Fe is presented where analyses permit

Figure 4 Bivariate plot of measured pore area against the Na content of dalyite within the pore

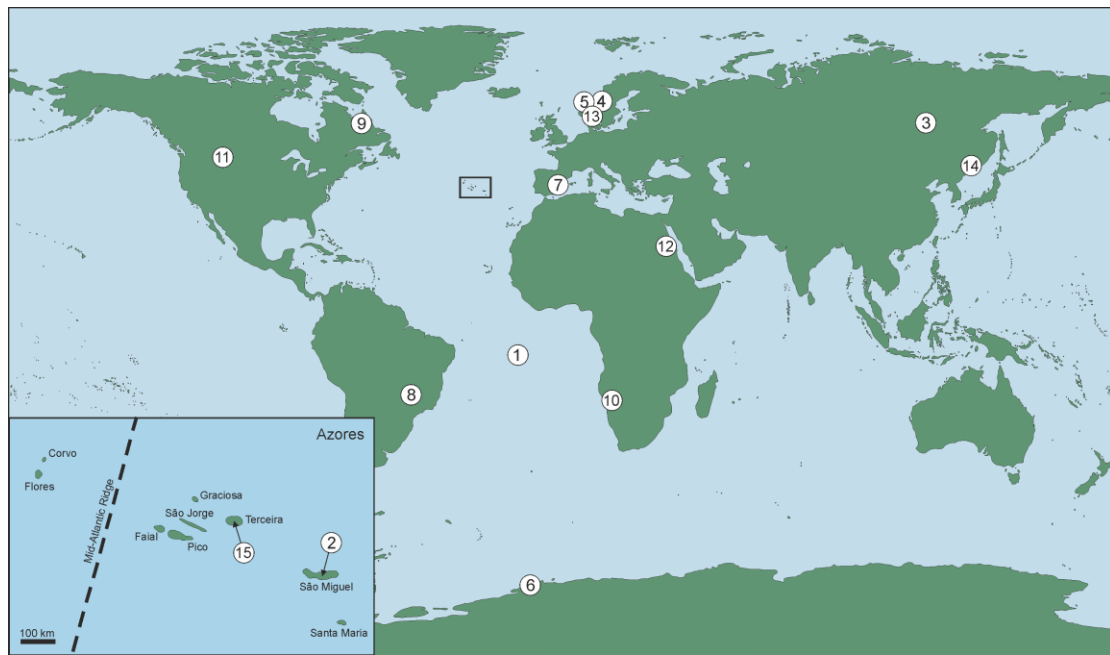


Figure 1

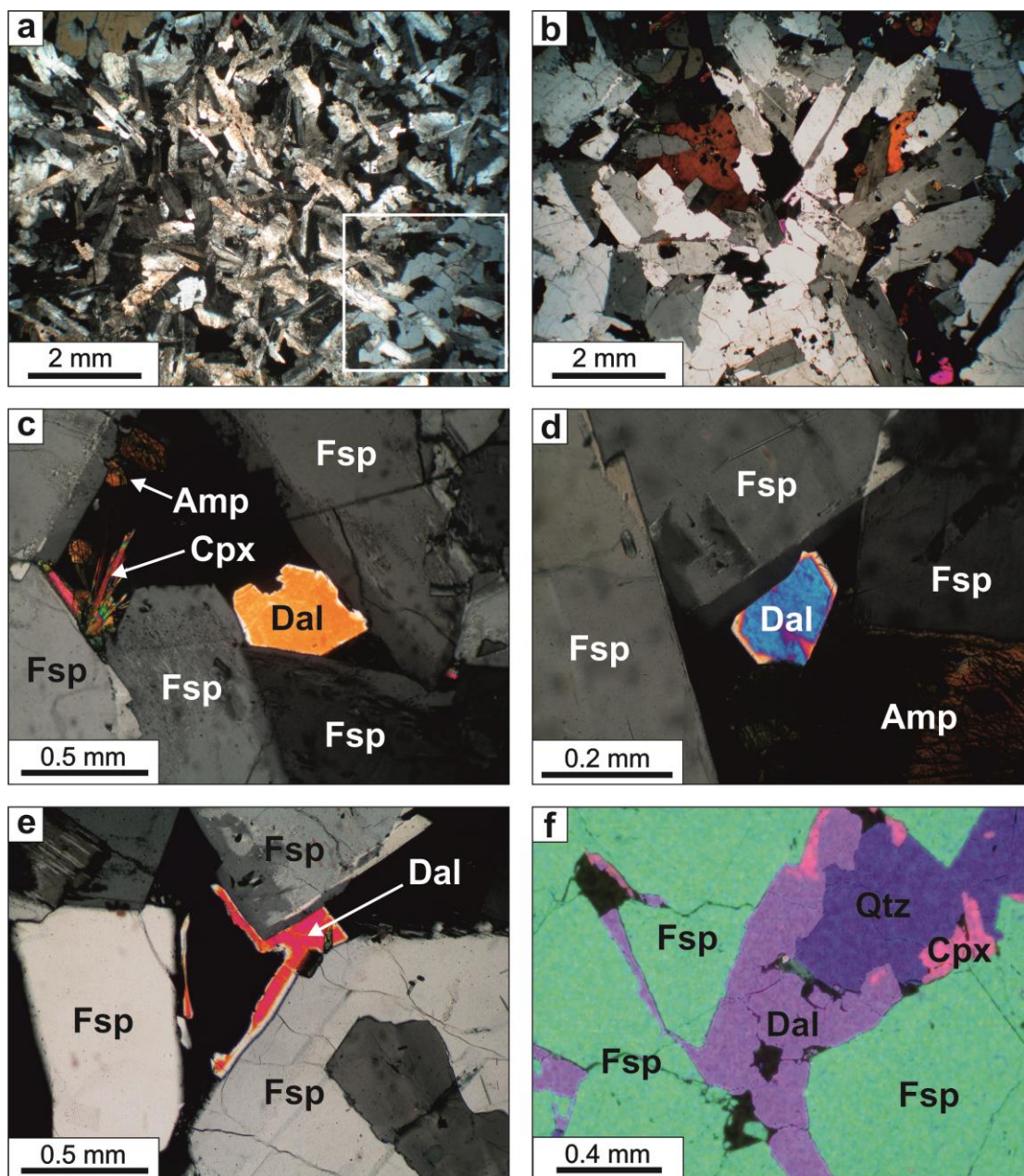


Figure 2

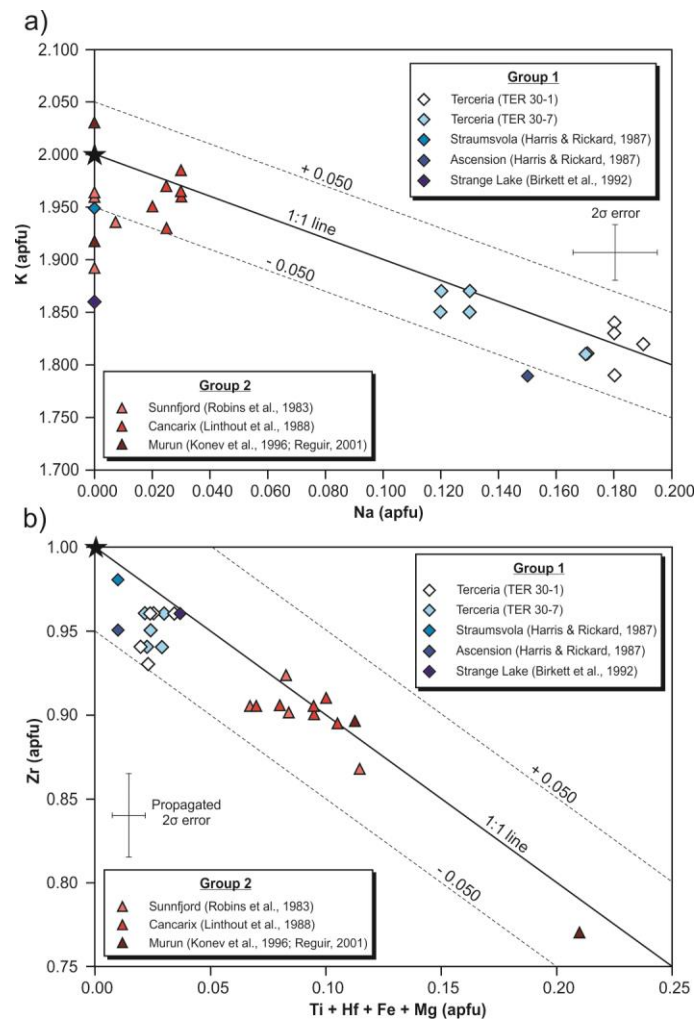


Figure 3

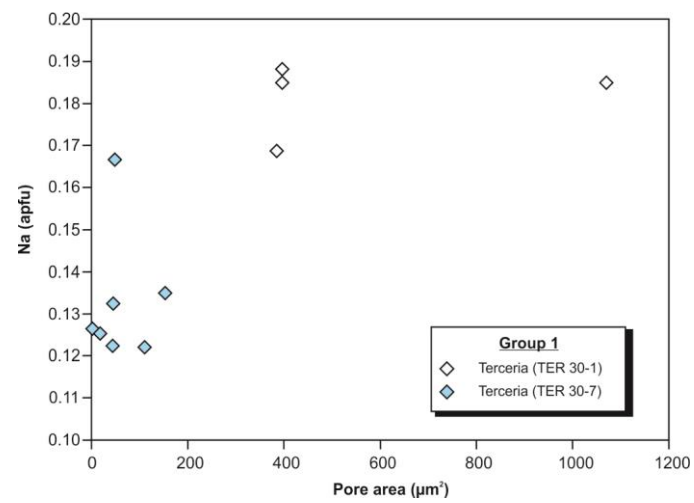


Figure 4

Table 1 Literature electron microprobe analyses of dalyite

Location Group	Ascension 1	Ascension 1	Straumsvola 1	Strange Lake 1	Gordon Butte 1	Agua de Pau 1	Agua de Pau 1	Agua de Pau 1	Agua de Pau 1
Host rock	Granite ejecta	Granite ejecta	Granite dyke	Granite	Alkaline pegmatite	Syenitic ejecta	Syenitic ejecta	Syenitic ejecta	Syenitic ejecta
Suggested origin	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic
No.	1 [†]	2*	3	4	5	6	7	8	9
SiO ₂	61.85	63.25	62.07	62.55	60.35	62.23	61.35	61.35	61.36
TiO ₂	-	0.12	0.13	0.08	1.78	0.08	0.11	0.14	0.15
Al ₂ O ₃	-	-	-	<i>bdl</i>	<i>bdl</i>	-	-	-	-
FeO	0.33	0.03	<i>bdl</i>	0.06	0.18	-	-	-	-
MnO	-	<i>bdl</i>	<i>bdl</i>	-	<i>bdl</i>	-	-	-	-
MgO	-	-	-	-	<i>bdl</i>	-	-	-	-
CaO	-	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	-	-	-	-
Na ₂ O	1.75	0.79	<i>bdl</i>	<i>bdl</i>	0.02	0.69	0.37	0.44	0.49
K ₂ O	14.60	14.63	15.71	15.08	15.34	13.80	14.56	14.60	14.72
ZrO ₂	21.70	20.43	20.63	20.38	18.21	23.72	23.57	23.27	23.49
HfO ₂	-	-	-	0.81	-	-	-	-	-
BaO	-	-	-	-	<i>bdl</i>	-	-	-	-
P ₂ O ₅	-	-	-	-	-	-	-	-	-
La ₂ O ₃	-	<i>bdl</i>	<i>bdl</i>	0.04	-	-	-	-	-
Ce ₂ O ₃	-	<i>bdl</i>	<i>bdl</i>	0.06	<i>bdl</i>	-	-	-	-
Nb ₂ O ₅	-	<i>bdl</i>	<i>bdl</i>	-	1.65	-	-	-	-
Total	100.23	99.25	98.54	98.96	97.53	100.52	99.96	99.80	100.21
Si	5.94	6.05	6.03	6.04	5.92	5.94	5.92	5.92	5.91
Ti	-	0.01	0.01	0.01	0.13	0.01	0.01	0.01	0.01
Al	-	-	-	<i>bdl</i>	<i>bdl</i>	-	-	-	-
Fe	0.03	0.00	<i>bdl</i>	0.01	0.02	-	-	-	-
Mn	-	<i>bdl</i>	<i>bdl</i>	-	<i>bdl</i>	-	-	-	-
Mg	-	-	-	-	<i>bdl</i>	-	-	-	-
Ca	-	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	-	-	-	-
Na	0.33	0.15	<i>bdl</i>	<i>bdl</i>	0.00	0.13	0.07	0.08	0.09
K	1.79	1.79	1.95	1.86	1.92	1.68	1.79	1.80	1.81
Zr	1.02	0.95	0.98	0.96	0.87	1.10	1.11	1.10	1.10
Hf	-	-	-	0.02	-	-	-	-	-
Ba	-	-	-	-	<i>bdl</i>	-	-	-	-
P	-	-	-	-	-	-	-	-	-
La	-	<i>bdl</i>	<i>bdl</i>	0.00	-	-	-	-	-
Ce	-	<i>bdl</i>	<i>bdl</i>	0.00	<i>bdl</i>	-	-	-	-
Nb	-	<i>bdl</i>	<i>bdl</i>	-	0.07	-	-	-	-
Sum	9.11	8.95	8.97	8.90	8.93	8.86	8.90	8.91	8.92
K _{alk}	23.27	21.68	21.74	20.90	21.50	20.43	20.90	21.10	21.30

Analysis 1-2 from Ascension Island, (van Tassel, 1952; Harris & Rickard, 1987), analysis 3 from Straumsvola, Antarctica (Harris & Rickard, 1987), analysis 4 from the Strange Lake complex, Canada (Birkett et al., 1992), analysis 5 from Gordon Butte, USA (Chakhmouradian & Mitchell, 2002), analyses 6-9 from Agua de Pau, São Miguel Island (Ridolfi et al., 2003), analyses 10-15 from the Murun complex, Russia (Lazebnik & Makhoto, 1982; Konev et al., 1996; Reguir, 2001), analyses 16-25 from Sunnfjord, Norway (Robins et al., 1983), , analyses 26-31 from Cancarix, Spain (Linthout et al., 1988). Abbreviations and symbols used: (-) = not analysed; † Analysis includes 0.64 wt. % H₂O; * Average of three analyses; bdl = below detection limit. K_{alk} calculated after Khomyakov, 1995. All structural formulae recalculated from reported weight percent oxide values

Table 1 continued

Location	Murun	Murun	Murun	Murun	Murun	Murun	Sunnfjord	Sunnfjord	Sunnfjord	Sunnfjord	Sunnfjord
Group	2	2	2	2	2	2	2	2	2	2	2
Host rock											
Suggested origin	Magmatic or Metasomatic	Magmatic or Metasomatic	Charoitite Magmatic or Metasomatic	Charoitite Magmatic or Metasomatic	Charoitite Magmatic or Metasomatic	Charoitite Magmatic or Metasomatic	Syenite dyke Magmatic	Syenite dyke Magmatic	Syenite dyke Magmatic	Syenite dyke Magmatic	Syenite dyke Magmatic
No.	10	11	12	13	14	15	16	17	18	19	20
SiO ₂	63.62	60.82	63.44	62.35	61.83	62.25	63.39	61.86	64.94	64.12	64.22
TiO ₂	1.87	0.69	2.92	5.86	0.69	1.56	0.64	1.22	1.59	0.83	0.88
Al ₂ O ₃	0.03	<i>bdl</i>	<i>bdl</i>	0.02	<i>bdl</i>	<i>bdl</i>	0.03	0.01	<i>bdl</i>	0.15	0.06
FeO	<i>bdl</i>	<i>bdl</i>	0.01	0.07	<i>bdl</i>	<i>bdl</i>	0.22	0.30	0.26	0.31	0.19
MnO	-	-	-	-	<i>bdl</i>	<i>bdl</i>	0.05	<i>bdl</i>	0.06	<i>bdl</i>	<i>bdl</i>
MgO	-	-	-	-	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	0.08	<i>bdl</i>	<i>bdl</i>	0.05
CaO	0.02	0.03	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	0.04	<i>bdl</i>	0.03	<i>bdl</i>	<i>bdl</i>
Na ₂ O	0.11	0.03	<i>bdl</i>	0.10	<i>bdl</i>	<i>bdl</i>	0.04	<i>bdl</i>	0.09	<i>bdl</i>	<i>bdl</i>
K ₂ O	14.99	15.41	16.75	16.68	15.15	15.65	15.93	16.64	14.08	15.80	16.36
ZrO ₂	21.50	22.16	16.68	14.84	20.60	19.13	19.49	18.83	19.13	20.17	19.68
HfO ₂	-	-	-	-	<i>bdl</i>	<i>bdl</i>	-	-	-	-	-
BaO	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	0.08	0.03	0.11	0.04	0.03
P ₂ O ₅	-	-	-	-	<i>bdl</i>	<i>bdl</i>	0.10	0.12	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
La ₂ O ₃	-	-	-	-	<i>bdl</i>	<i>bdl</i>	-	-	-	-	-
Ce ₂ O ₃	-	-	-	-	<i>bdl</i>	<i>bdl</i>	-	-	-	-	-
Nb ₂ O ₅	-	-	-	-	<i>bdl</i>	0.60	-	-	-	-	-
Total	102.14	99.14	99.79	99.92	98.27	99.19	100.01	99.09	100.29	101.42	101.47
Si	5.94	5.92	6.01	5.89	6.00	5.98	6.04	5.98	6.08	6.02	6.03
Ti	0.13	0.05	0.21	0.42	0.05	0.11	0.05	0.09	0.11	0.06	0.06
Al	0.00	<i>bdl</i>	<i>bdl</i>	0.00	<i>bdl</i>	<i>bdl</i>	0.00	0.00	<i>bdl</i>	0.02	0.01
Fe	<i>bdl</i>	<i>bdl</i>	0.00	0.01	<i>bdl</i>	<i>bdl</i>	0.02	0.02	0.02	0.02	0.01
Mn	-	-	-	-	<i>bdl</i>	<i>bdl</i>	0.00	<i>bdl</i>	0.00	<i>bdl</i>	<i>bdl</i>
Mg	-	-	-	-	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	0.01	<i>bdl</i>	<i>bdl</i>	0.01
Ca	0.00	0.00	<i>bdl</i>	-	<i>bdl</i>	<i>bdl</i>	0.00	<i>bdl</i>	0.00	<i>bdl</i>	<i>bdl</i>
Na	0.02	0.01	<i>bdl</i>	0.02	<i>bdl</i>	<i>bdl</i>	0.01	<i>bdl</i>	0.02	<i>bdl</i>	<i>bdl</i>
K	1.78	1.91	2.03	2.01	1.88	1.92	1.94	2.05	1.68	1.89	1.96
Zr	0.98	1.05	0.77	0.68	0.98	0.90	0.91	0.89	0.87	0.92	0.90
Hf	-	-	-	-	<i>bdl</i>	<i>bdl</i>	-	-	-	-	-
Ba	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	0.00	0.00	0.00	0.00	0.00
P	-	-	-	-	<i>bdl</i>	<i>bdl</i>	0.01	0.01	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
La	-	-	-	-	<i>bdl</i>	<i>bdl</i>	-	-	-	-	-
Ce	-	-	-	-	<i>bdl</i>	<i>bdl</i>	-	-	-	-	-
Nb	-	-	-	-	<i>bdl</i>	0.03	-	-	-	-	-
Sum	8.85	8.94	9.02	9.03	8.91	8.93	8.97	9.05	8.79	8.94	8.98
K _{alk}	20.34	21.48	22.51	22.48	21.07	21.47	21.71	22.65	19.34	21.16	21.80

Table 1 continued

Location Group Host rock Suggested origin No.	Sunnfjord 2 Syenite dyke Magmatic 21	Sunnfjord 2 Syenite dyke Magmatic 22	Sunnfjord 2 Syenite dyke Magmatic 23	Sunnfjord 2 Syenite dyke Magmatic 24	Sunnfjord 2 Syenite dyke Magmatic 25	Cancarix 2 Lamproite Magmatic 26	Cancarix 2 Lamproite Magmatic 27	Cancarix 2 Lamproite Magmatic 28	Cancarix 2 Lamproite Magmatic 29	Cancarix 2 Lamproite Magmatic 30	Cancarix 2 Lamproite Magmatic 31
SiO ₂	62.75	62.25	62.53	62.58	62.04	62.60	62.45	62.65	62.95	62.65	63.00
TiO ₂	1.08	1.54	1.21	1.61	1.71	1.25	1.10	1.10	0.75	1.15	0.85
Al ₂ O ₃	0.01	0.13	0.12	0.07	0.03	0.10	0.10	0.10	0.05	0.05	0.05
FeO	0.60	0.31	0.19	0.15	0.28	0.18	0.18	0.18	0.18	0.09	0.18
MnO	0.04	0.05	bdl	bdl	0.03	bdl	-	-	-	-	-
MgO	0.65	0.10	0.08	0.02	0.06	bdl	bdl	-	0.05	bdl	0.05
CaO	0.04	0.04	0.06	bdl	0.02	bdl	-	-	-	-	-
Na ₂ O	bdl	0.19	bdl	bdl	0.07	0.15	0.15	0.15	0.10	0.15	0.15
K ₂ O	15.79	15.33	15.98	16.17	13.93	15.75	16.10	16.10	15.95	16.25	16.10
ZrO ₂	18.29	19.22	18.46	20.23	20.16	19.10	19.20	19.35	19.40	19.60	19.70
HfO ₂	-	-	-	-	-	-	-	-	-	-	-
BaO	bdl	0.19	0.21	0.20	0.22	0.45	0.30	0.40	0.15	0.25	0.35
P ₂ O ₅	0.04	0.10	bdl	bdl	bdl	-	-	-	-	-	-
La ₂ O ₃	-	-	-	-	-	-	-	-	-	-	-
Ce ₂ O ₃	-	-	-	-	-	-	-	-	-	-	-
Nb ₂ O ₅	-	-	-	-	-	-	-	-	-	-	-
Total	99.29	99.45	98.84	101.03	98.55	99.58	99.58	100.03	99.58	100.19	100.43
Si	6.01	5.97	6.02	5.94	5.97	6.00	6.00	6.00	6.02	5.99	6.00
Ti	0.08	0.11	0.09	0.11	0.12	0.09	0.08	0.08	0.05	0.09	0.06
Al	0.00	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01
Fe	0.05	0.02	0.02	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Mn	0.00	0.00	bdl	bdl	0.00	bdl	-	-	-	-	-
Mg	0.09	0.01	0.01	0.00	0.01	bdl	bdl	-	0.01	bdl	0.01
Ca	0.00	0.00	0.01	bdl	0.00	bdl	-	-	-	-	-
Na	bdl	0.04	bdl	bdl	0.01	0.03	0.03	0.03	0.02	0.03	0.03
K	1.93	1.87	1.96	1.96	1.71	1.93	1.97	1.97	1.95	1.99	1.96
Zr	0.85	0.90	0.87	0.94	0.95	0.90	0.90	0.91	0.91	0.91	0.91
Hf	-	-	-	-	-	-	-	-	-	-	-
Ba	bdl	0.01	0.01	0.01	0.01	0.02	0.01	0.02	0.01	0.01	0.01
P	0.00	0.01	0.00	bdl	bdl	-	-	-	-	-	-
La	-	-	-	-	-	-	-	-	-	-	-
Ce	-	-	-	-	-	-	-	-	-	-	-
Nb	-	-	-	-	-	-	-	-	-	-	-
Sum	9.02	8.96	9.00	8.98	8.82	8.99	9.02	9.01	8.99	9.02	9.01
K _{alk}	21.42	21.29	21.78	21.80	19.55	21.83	22.20	22.17	21.89	22.28	22.06

Table 2 Average detection limits and errors for Terceira dalyite analyses

	Detection limit (wt. %)	Oxide error (wt. %)	Formula error (apfu)
SiO ₂	0.034	0.326	0.045
TiO ₂	0.038	0.054	0.004
Al ₂ O ₃	0.020	0.027	0.003
Cr ₂ O ₃	0.023	bdl	bdl
FeO	0.038	0.052	0.004
MnO	0.022	0.030	0.002
MgO	0.020	0.024	0.003
CaO	0.024	bdl	bdl
Na ₂ O	0.046	0.078	0.015
K ₂ O	0.021	0.199	0.026
ZrO ₂	0.062	0.524	0.025
HfO ₂	0.032	0.055	0.002
BaO	0.045	0.073	0.003
Total		0.661	

bdl = all values below detection limit

Table 3 Comparison of experimental and calculated lattice parameters

Lattice parameter	Experimental	Calculated	% difference
a/Å	7.371	7.211	-2.17
b/Å	7.730	7.679	-0.66
c/Å	6.912	6.787	-1.80
β /degrees	106.23	104.82	-1.33

Table 4 Whole rock major element analyses of the CCI syenite ejecta

Sample	TER 30-1	TER 35-1	TER 30-6	TER 30-7
SiO ₂	64.14	64.78	63.90	64.80
TiO ₂	0.58	0.45	0.61	0.41
Al ₂ O ₃	15.76	15.51	15.82	16.18
Fe ₂ O ₃	5.34	5.29	5.57	4.53
MnO	0.21	0.20	0.22	0.17
MgO	0.36	0.27	0.36	0.27
CaO	0.82	0.44	0.76	0.54
Na ₂ O	7.44	7.41	7.36	7.25
K ₂ O	4.93	5.11	4.98	5.10
P ₂ O ₅	0.08	0.06	0.07	0.05
LOI	0.10	0.30	0.10	0.40
Total	99.76	99.82	99.75	99.70
A.I.	1.12	1.14	1.11	1.08
Na ₂ O/K ₂ O	1.51	1.45	1.48	1.42
CIPW				
Q	1.52	3.33	1.00	2.42
Or	29.25	30.32	29.55	30.14
Ab	53.76	51.58	53.84	54.83
An	0.00	0.00	0.00	0.00
Di	3.08	1.57	2.88	2.06
Hy	4.40	5.05	4.54	5.55
Ac	6.02	5.64	6.10	2.05
Il	1.10	0.85	1.16	0.78
Ap	0.19	0.14	0.16	0.12
NaS	0.61	1.18	0.41	0.97

Table 5 Electron microprobe analyses of dalyite from CCI syenite ejecta

Sample Group	TER 30-1 1	TER 30-1 1	TER 30-1 1	TER 30-1 1	TER 30-1 1	TER 30-7 1	TER 30-7 1	TER 30-7 1	TER 30-7 1	TER 30-7 1	TER 30-7 1	TER 30-7 1
Suggested origin	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic
SiO ₂	62.9	62.6	62.4	62.2	62.4	62.9	63.0	62.4	62.6	62.6	63.0	63.0
TiO ₂	0.10	0.23	0.19	0.13	0.11	0.17	0.10	0.12	0.41	0.09	0.06	0.27
Al ₂ O ₃	<i>bdl</i>	<i>bdl</i>	0.03	0.03	<i>bdl</i>	<i>bdl</i>	0.04	0.04	0.05	0.03	<i>bdl</i>	<i>bdl</i>
Cr ₂ O ₃	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
FeO	<i>bdl</i>	0.06	<i>bdl</i>	0.06	0.09	<i>bdl</i>	0.07	0.07	0.11	0.05	0.06	<i>bdl</i>
MnO	<i>bdl</i>	0.03	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	0.04	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
MgO	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	0.03	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
CaO	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
Na ₂ O	0.99	0.95	0.99	1.00	0.90	0.90	0.67	0.71	0.67	0.72	0.66	0.66
K ₂ O	14.6	15.0	14.9	14.8	14.7	14.8	15.0	15.0	15.0	15.2	15.3	15.1
ZrO ₂	20.0	20.5	19.8	20.4	20.4	20.4	19.7	20.3	19.1	20.0	20.6	20.2
HfO ₂	0.46	0.40	0.38	0.40	0.39	0.45	0.39	0.39	0.42	0.42	0.48	0.38
BaO	0.06	0.06	0.08	<i>bdl</i>	<i>bdl</i>	0.05	0.08	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
Total	99.08	99.78	98.81	98.89	98.98	99.72	98.99	99.05	98.33	99.01	100.17	99.57
Si	6.05	6.01	6.03	6.01	6.02	6.03	6.06	6.02	6.05	6.04	6.02	6.04
Ti	0.007	0.016	0.013	0.009	0.008	0.012	0.008	0.009	0.030	0.006	0.004	0.019
Al	<i>bdl</i>	<i>bdl</i>	0.004	0.003	<i>bdl</i>	<i>bdl</i>	0.005	0.004	0.006	0.004	<i>bdl</i>	<i>bdl</i>
Cr	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
Fe	<i>bdl</i>	0.005	<i>bdl</i>	0.004	0.007	<i>bdl</i>	0.005	0.006	0.009	0.004	0.005	<i>bdl</i>
Mn	<i>bdl</i>	0.002	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	0.004	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
Mg	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	0.004	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
Ca	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
Na	0.18	0.18	0.18	0.19	0.17	0.17	0.13	0.13	0.13	0.13	0.12	0.12
K	1.79	1.84	1.83	1.82	1.81	1.81	1.84	1.85	1.85	1.87	1.87	1.85
Zr	0.94	0.96	0.93	0.96	0.96	0.95	0.92	0.96	0.90	0.94	0.96	0.94
Hf	0.013	0.011	0.010	0.011	0.011	0.012	0.011	0.011	0.011	0.012	0.013	0.010
Ba	0.002	0.002	0.003	<i>bdl</i>	<i>bdl</i>	0.002	0.003	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
Sum	8.982	9.026	9.000	9.007	8.986	8.986	8.982	8.994	8.990	9.006	8.992	8.979
K _{alk}	21.98	22.34	22.39	22.32	22.06	21.99	21.90	22.03	21.98	22.27	22.13	21.94

Table 6 Results of computer modelling undertaken using the GULP code (Gale, 1997)

Substitution	Solution scheme	E _{sol} (eV)
Ti → Zr	TiO ₂ + Zr _{Zr} → Ti _{Zr} + ZrO ₂	-0.25
Ti → Si	TiO ₂ + Si _{Si} → Ti _{Si} + SiO ₂	-0.98
Ti → K	TiO ₂ + 4K _K → Ti _K ^{•••} + 3V _K ['] + 2K ₂ O	30.64
Hf → Zr	HfO ₂ + Zr _{Zr} → Hf _{Zr} + ZrO ₂	-0.31
Hf → Si	HfO ₂ + Si _{Si} → Hf _{Si} + SiO ₂	2.67
Hf → K	HfO ₂ + 4K _K → Hf _K ^{•••} + 3V _K ['] + 2K ₂ O	29.09
Fe ²⁺ → Zr	FeO + Zr _{Zr} → Fe _{Zr} ^{''} + V _O ^{••} + ZrO ₂	12.52
Fe ²⁺ → Si	FeO + Si _{Si} → Fe _{Si} ^{''} + V _O ^{••} + SiO ₂	13.69
Fe ²⁺ → K	FeO + K _K → Fe _K [•] + V _K ['] + K ₂ O	8.86
Mg ²⁺ → Zr	MgO + Zr _{Zr} → Mg _{Zr} ^{''} + V _O ^{••} + ZrO ₂	12.97
Mg ²⁺ → Si	MgO + Si _{Si} → Mg _{Si} ^{''} + V _O ^{••} + SiO ₂	14.07
Mg ²⁺ → K	MgO + K _K → Mg _K [•] + V _K ['] + K ₂ O	9.61
Ba ²⁺ → Zr	BaO + Zr _{Zr} → Ba _{Zr} ^{''} + V _O ^{••} + ZrO ₂	12.54
Ba ²⁺ → Si	BaO + Si _{Si} → Ba _{Si} ^{''} + V _O ^{••} + SiO ₂	16.58
Ba ²⁺ → K	BaO + K _K → Ba _K [•] + V _K ['] + K ₂ O	4.94